

## Electronic Supplementary Information

### **Synthesis of chemisorbed imidazolium and phosphonium cations by reaction of ionic liquid precursors with silica**

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## **Experimental**

### ***General***

All reactions and manipulations were carried out under argon atmosphere. Toluene and *n*-hexane were dried over sodium, dichloromethane over CaH<sub>2</sub> and freshly distilled before use. 1,3-dimethylimidazolium-2-carboxylate (**1**), 1-butyl-3-methylimidazolium-2-yliden (**2**), 1-butyl-2-methylidene-3-methylimidazoline (**3**), and tri-*n*-butylmethylidenphosphorane (**3**) were synthesised according to the literature.<sup>1-3</sup> 1,3-dimethylimidazolium chloride (TCI), 1-butyl-3-methylimidazolium chloride (Aldrich), 1-butyl-2,3-dimethylimidazolium chloride (Merck), tri-*n*-butylmethylphosphonium iodide (TCI) and tri-*n*-butylmethylphosphonium chloride (TCI) were used as received. Aerosil<sup>®</sup>300 (BET = 260 m<sup>2</sup> g<sup>-1</sup>, 2.2 silanol groups per nm<sup>2</sup>) was supplied by Evonik, Hanau, Germany. The pyrogenic silica was heated at 350 °C and 3 mbar for 5 h to remove adsorbed water. All other chemicals used were purchased from Sigma-Aldrich, Acros, or Merck and purified according to standard procedures.

### ***Solid state NMR spectroscopy***

Solid state NMR experiments were performed at 9.4 T on a Bruker Digital Avance 400 spectrometer equipped with 7 mm (<sup>29</sup>Si-<sup>1</sup>H}-CP-MAS) and 4 mm (<sup>1</sup>H-, <sup>31</sup>P-<sup>1</sup>H}-HR-MAS, <sup>13</sup>C-<sup>1</sup>H}-CP-MAS) double-tuned probes capable of MAS (magic angle spinning). To enhance sensitivity of <sup>29</sup>Si and <sup>13</sup>C solid state NMR cross polarization from <sup>1</sup>H was used. <sup>1</sup>H and <sup>31</sup>P NMR experiments were performed using special 4mm ZrO HR-MAS rotors with a teflon spacer. The solid samples were dispersed in dichloromethane-*d*<sub>2</sub> or benzene-*d*<sub>6</sub> and transferred into the rotor under an inert atmosphere. <sup>1</sup>H decoupling using a tppm15 pulse sequence was performed during acquisition for <sup>13</sup>C, <sup>29</sup>Si, and <sup>31</sup>P experiments. Chemical shifts are referenced to the δ-scale.

#### *<sup>29</sup>Si-<sup>1</sup>H}-CP-MAS*

Spinning rate: 5 kHz

CP contact time: 3 ms

Recycle delay: 5 s

Reference: tetrakis(trimethylsilyl)silane, -9.8 and -125.2 ppm (external standard)

#### *<sup>13</sup>C-<sup>1</sup>H}-CP-MAS*

Spinning rate: 12.5 kHz

CP contact time: 3 ms

Recycle delay: 5 s

Reference: adamantane, 38.48 ppm (external standard)

#### *<sup>1</sup>H-HR-MAS*

Spinning rate: 10 kHz

90 ° pulse: 5.5 μs

Recycle delay: 6 s

Reference: dichloromethane-*d*<sub>2</sub>, 5.31 ppm (internal standard)

### $^{31}\text{P}$ - $\{^1\text{H}\}$ -HR-MAS

Spinning rate: 10 kHz

90 ° pulse: 4  $\mu\text{s}$

Recycle delay: 5 s

Reference:  $\text{H}_3\text{PO}_4$  (85% in water), 0 ppm (external standard)

### **Quantitative Elemental Analysis**

Quantitative elemental analyses (C, H, N) were performed with a Vario EL from Elementar Analysensysteme GmbH Hanau.

### **Synthesis of [Mmim]<sup>+</sup>Aero<sup>-</sup>**

1.494 g (24.9 mmol) Aerosil<sup>®</sup>300 was dispersed in a solution of 0.447 g (3.2 mmol) 1,3-dimethylimidazolium-2-carboxylate in 150 mL dichloromethane and stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the white solid was again dispersed in 40 mL toluene and the mixture was refluxed for 2 h with an oil bath temperature of 140 °C. The pale yellow dispersion was centrifuged at 8,500 rpm for 15 min. The precipitate was washed (suspended and centrifuged) ten times with 50 mL dichloromethane. The product was dried at 50 °C for 5 h under reduced pressure. A pale yellow solid was obtained.

CHN-Analysis: C = 4.90 %, H = 1.11 %, N = 2.41 %

### **Synthesis of [Bmim]<sup>+</sup>Aero<sup>-</sup>**

1.601 g (26.6 mmol) Aerosil<sup>®</sup>300 was dispersed in 40 mL *n*-Hexane and 0.372 g (2.7 mmol) 1-butyl-3-methylimidazolium-2-yliden was added at room temperature under vigorous stirring and furthermore stirred for 12 h. The obtained light orange dispersion was centrifuged at 8,500 rpm for 15 min. The precipitate was washed (suspended and centrifuged) ten times with 50 mL dichloromethane. The product was dried at 50 °C for 5 h under reduced pressure. A pale yellow solid was obtained.

CHN-Analysis: C = 6.25 %, H = 1.26 %, N = 2.08 %

### **Synthesis of [Bdmim]<sup>+</sup>Aero<sup>-</sup>**

1.508 g (25.1 mmol) Aerosil<sup>®</sup>300 was dispersed in 40 mL *n*-Hexane and 0.502 g (3.3 mmol) 1-butyl-2-methylidene-3-methylimidazoline was added at room temperature under vigorous stirring and furthermore stirred for 12 h. The obtained light orange dispersion was centrifuged at 8,500 rpm for 15 min. The precipitate was washed (suspended and centrifuged) ten times with 50 mL dichloromethane. The product was dried at 50 °C for 5 h under reduced pressure. A pale yellow solid was obtained.

CHN-Analysis: C = 6.50 %, H = 1.22 %, N = 2.01 %

### ***Synthesis of [TbmP]<sup>+</sup>Aero<sup>-</sup>***

1.493 g (24.9 mmol) Aerosil<sup>®</sup>300 was dispersed in 40 mL *n*-Hexane and 0.699 g (3.2 mmol) tri-*n*-butylmethylidene phosphorane was added at room temperature under vigorous stirring and furthermore stirred for 12 h. The obtained colourless dispersion was centrifuged at 8,500 rpm for 15 min. The precipitate was washed (suspended and centrifuged) five times with 50 mL *n*-hexane and five times with 50 mL dichloromethane. The product was dried at 50 °C for 5 h under reduced pressure. A white solid was obtained.

CHN-Analysis: C = 5.28 %, H = 1.28 %

### ***Adsorption of 1,3-dimethylimidazolium chloride ([Mmim]Cl) onto Aerosil<sup>®</sup>300***

0.0465 g (0.35 mmol) 1,3-dimethylimidazolium chloride was dissolved in 20 mL dried dichloromethane and added to a dispersion of 0.4627 g (7.7 mmol) Aerosil<sup>®</sup>300 in 10 mL dichloromethane. The dispersion was stirred for 1 h and the solvent was removed under reduced pressure. The obtained white solid was dried at 50 °C at 3 mbar for 3 h.

### ***Adsorption of 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) onto Aerosil<sup>®</sup>300***

0.0627 g (0.36 mmol) 1-butyl-3-methylimidazolium chloride was dissolved in 20 mL dried dichloromethane and added to a dispersion of 0.4718 g (7.9 mmol) Aerosil<sup>®</sup>300 in 10 mL dichloromethane. The dispersion was stirred for 1 h and the solvent was removed under reduced pressure. The obtained white solid was dried at 50 °C at 3 mbar for 3 h.

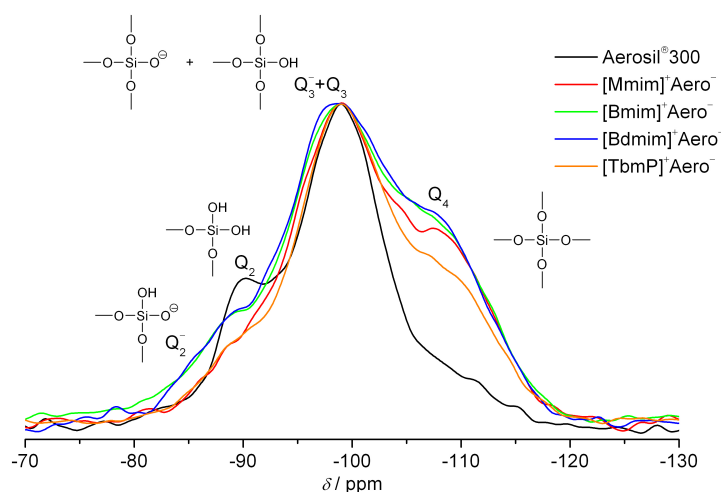
### ***Adsorption of 1-butyl-2,3-dimethylimidazolium chloride ([Bdmim]Cl) onto Aerosil<sup>®</sup>300***

0.0732 g (0.39 mmol) 1-butyl-2,3-dimethylimidazolium chloride was dissolved in 20 mL dried dichloromethane and added to a dispersion of 0.5125 g (8.5 mmol) Aerosil<sup>®</sup>300 in 10 mL dichloromethane. The dispersion was stirred for 1 h and the solvent was removed under reduced pressure. The obtained white solid was dried at 50 °C at 3 mbar for 3 h.

### ***Adsorption of tri-*n*-butylmethylphosphonium chloride ([TbmP]Cl) onto Aerosil<sup>®</sup>300***

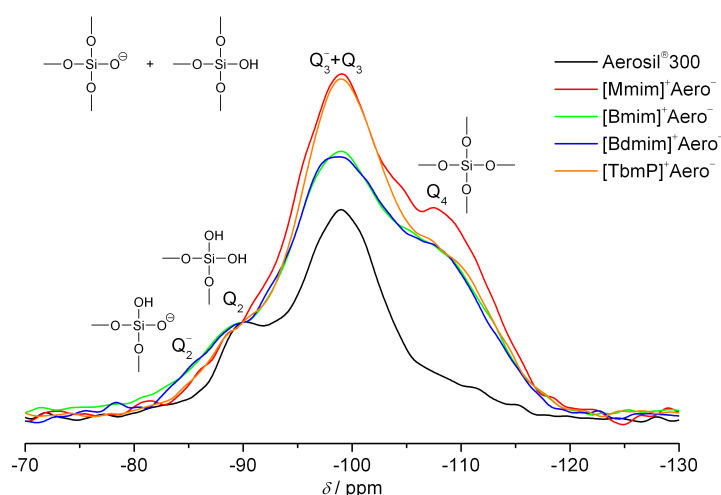
0.0821 g (0.33 mmol) tri-*n*-butylmethylphosphonium chloride was dissolved in 20 mL dried dichloromethane and added to a dispersion of 0.4374 g (7.3 mmol) Aerosil<sup>®</sup>300 in 10 mL dichloromethane. The dispersion was stirred for 1 h and the solvent was removed under reduced pressure. The obtained white solid was dried at 50 °C at 3 mbar for 3 h.

## NMR Spectra



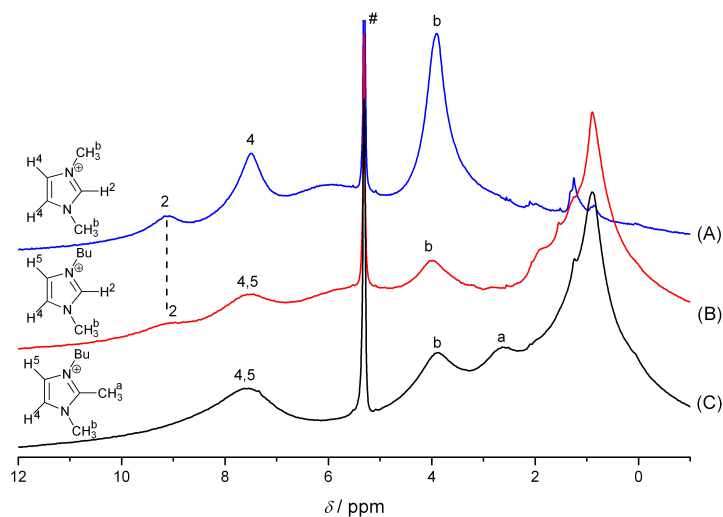
**Fig. S1**  $^{29}\text{Si}\{-^1\text{H}\}$ -CP-MAS NMR spectra of pure Aerosil<sup>®</sup>300 and the products of the IL precursor/Aerosil<sup>®</sup>300 reactions. The spectra are normalized to the intensity of the  $\text{Q}_3$  ( $\text{Q}_3^-$ ) signals.

The  $^{29}\text{Si}\{-^1\text{H}\}$ -CP-MAS NMR spectra are the same like in Figure 1 in the article, but in this case normalized to the intensity of the  $\text{Q}_3$  ( $\text{Q}_3^-$ ) signals. This was performed to show that the  $\text{Q}_3$  peaks of the products are broadened and the maxima slightly shifted downfield in comparison to the pure Aerosil<sup>®</sup>300.

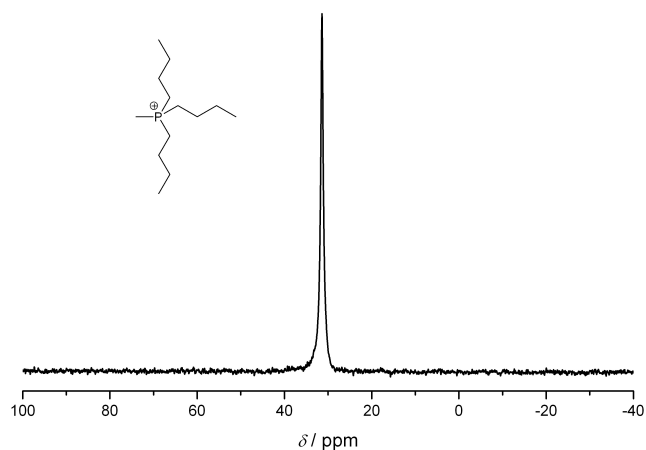


**Fig. S2**  $^{29}\text{Si}\{-^1\text{H}\}$ -CP-MAS NMR spectra of pure Aerosil<sup>®</sup>300 and the products of the IL precursor/Aerosil<sup>®</sup>300 reactions. The spectra are normalized to the intensity of the  $\text{Q}_2$  signal at  $-90$  ppm.

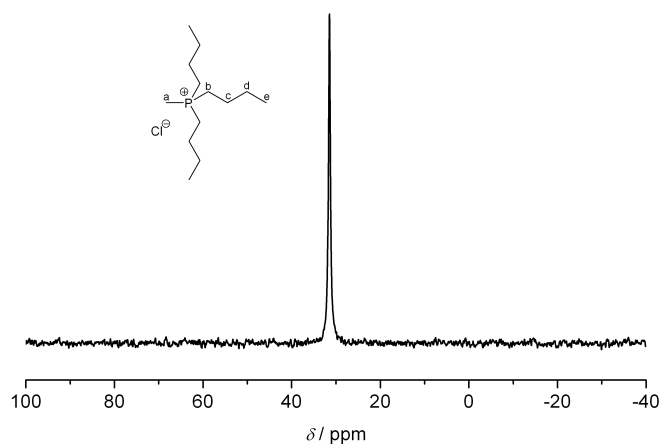
The  $^{29}\text{Si}\{-^1\text{H}\}$ -CP-MAS NMR spectra are the same as in Figure 1 in the article and Figure S1 in the ESI, but in this case normalized to the intensity of the  $\text{Q}_2$  signal at  $-90$  ppm. This plot was chosen to compare the signals of the geminal silanol groups and to show the appearance of a shoulder at about  $-87$  ppm, which could be assigned to geminal silanolate groups ( $\text{Q}_2^-$ ). The intensity of this peak varies for the products due to possible proton exchange processes with neighbouring silanol groups.



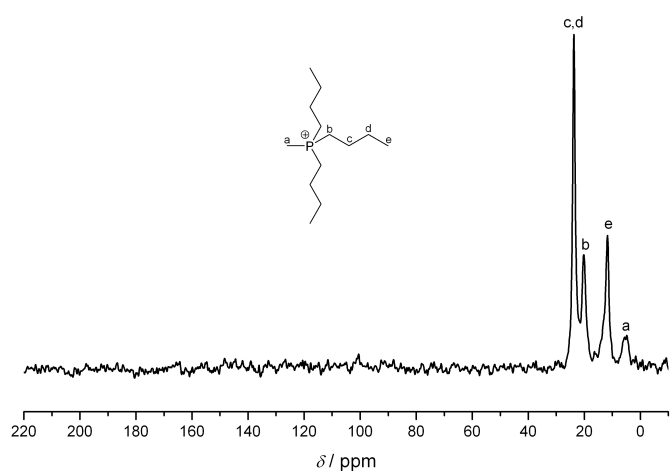
**Fig. S3**  $^1\text{H}$ -HR-MAS NMR spectra of (A)  $[\text{Mmim}]^+\text{Aero}^-$ , (B)  $[\text{Bmim}]^+\text{Aero}^-$ , and (C)  $[\text{Bdmim}]^+\text{Aero}^-$  (Bu = *n*-butyl, # = solvent residual peak) measured in  $\text{CD}_2\text{Cl}_2$ .



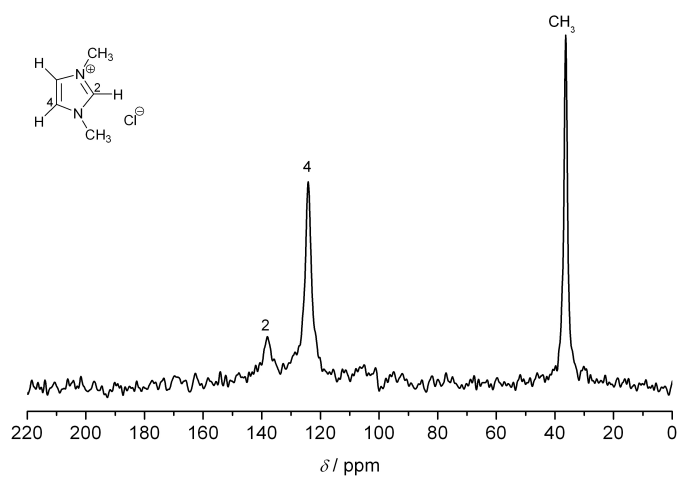
**Fig. S4**  $^{31}\text{P}$ - $\{^1\text{H}\}$ -HR-MAS NMR spectra of  $[\text{TbmP}]^+\text{Aero}^-$  measured in  $\text{C}_6\text{D}_{12}$ .



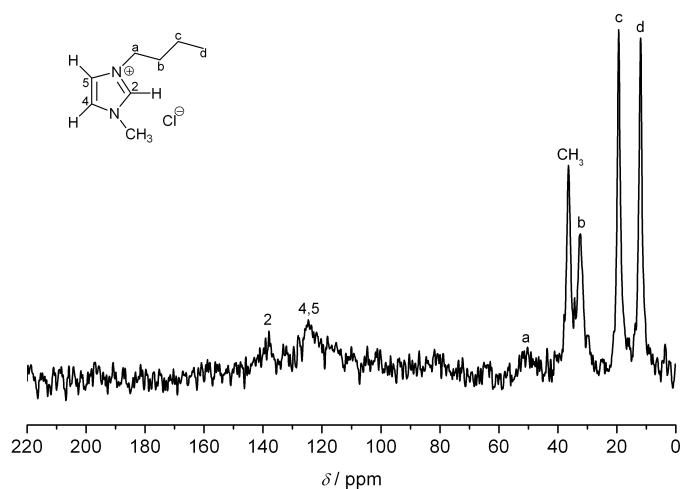
**Fig. S5**  $^{31}\text{P}$ - $\{^1\text{H}\}$ -HR-MAS NMR spectra of  $[\text{TbmP}]\text{Cl}$  adsorbed onto Aerosil<sup>®</sup>300 measured in  $\text{C}_6\text{D}_{12}$ .



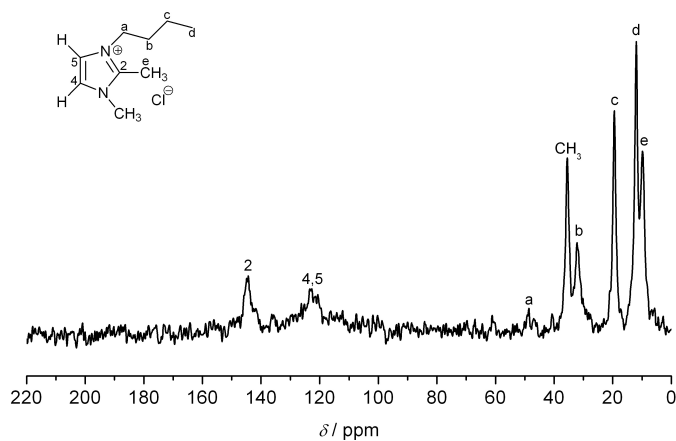
**Fig. S6** <sup>13</sup>C-<sup>1</sup>H}-CP-MAS NMR spectra of [TbmP]<sup>+</sup>Aero<sup>-</sup>.



**Fig. S7** <sup>13</sup>C-<sup>1</sup>H}-CP-MAS NMR spectra of [Mmim]Cl adsorbed onto Aerosil<sup>®</sup> 300.



**Fig. S8** <sup>13</sup>C-<sup>1</sup>H}-CP-MAS NMR spectra of [Bmim]Cl adsorbed onto Aerosil<sup>®</sup> 300.



**Fig. S9**  $^{13}\text{C}\{-^1\text{H}\}$ -CP-MAS NMR spectra of [Bdmim]Cl adsorbed onto Aerosil<sup>®</sup> 300.

### References

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- 2 Th. Linder and J. Sundermeyer, *Chem. Commun.*, 2009, 2914–2916.
- 3 R. Köster, D. Simić and M. A. Grassberger, *Liebigs Ann. Chem.*, 1970, **739**, 211–219.